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Procedia Chemistry 7 (2012) 334 – 340

Procedia Chemistry

ATALANTE 2012
International Conference on Nuclear Chemistry for Sustainable Fuel Cycles

A comparison of low and high LET (linear energy transfer) induced radiolysis of solvent extraction processes

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Abstract

Reagents used in chemical separation processes for used nuclear fuel are susceptible to radiolysis. Here we investigate the $^{10}B(n,\alpha)^{7}Li$ reaction for inducing high linear energy transfer (LET) radiolysis. A solution of tributyl phosphate (TBP) in n-dodecane, representing the PUREX solvent, was irradiated by gamma rays from a ^{137}Cs source and by high LET particles from the $^{10}B(n,\alpha)^{7}Li$ reaction in the UC Irvine TRIGA reactor. TBP degradation and Dibutyl phosphate (DBP) formation were quantified by gas chromatography. Our data show a significantly larger formation of DBP in the presence of gamma radiation compared to high LET radiation.

Keywords: alpha radiolysis; high linear energy transfer; tributyl phosphate, solvent extraction

1. Introduction

The increasing potential for adoption of nuclear energy as a mainstream replacement for a dwindling supply of fossil fuels depends largely on our ability to streamline and increase efficiencies of nuclear fuel cycles. At the same time we want to be able to reduce the toxicity of spent nuclear fuel which may be realized through partitioning and transmutation of transuranics and long lived fission products. Although it is not the only method

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doi:10.1016/j.proche.2012.10.053

for used fuel separation processes, solvent extraction has been utilized for decades and is used in commercial plants such as La Hague in France or Sellafield in the UK.

The PUREX process (or advanced adaptations of PUREX) is already used at the industrial scale to recycle usable uranium and plutonium while a multitude of other unique solvent extraction processes are under development at lab and pilot scale for partitioning of spent nuclear fuel. Extraction reagents utilized in all of these processes are not immune to the harsh chemical environment they are exposed to which includes radiolysis and acid and metal ion hydrolysis. Partial destruction of these ligands leads to reduction in process efficiency and selectivity. Candidate ligands must be screened for susceptibility to these types of attack in order to assess viability for economical application in an extraction process.

In light of this many studies have been performed assessing the impact of gamma radiation on tributyl phosphate (TBP), the extraction reagent utilized in the PUREX process, and these findings have been reported recently in a review by Mincher et al. [1]. Very little work has been performed to study the effect of alpha radiation on TBP and other solvent extraction reagents. This has not been due to a smaller relative importance or abundance of alpha emitters present in used nuclear fuel compared to gamma emitters, but rather due to the difficulty in studying alpha radiation. Examples where alpha radiolysis has been studied include helium ion beam [2] and addition of radioactive alpha emitters to a sample [3].

The effects of gamma irradiation and alpha irradiation on extraction reagents may vary due to their difference in linear energy transfer (LET) which describes the rate at which their energy is deposited in matter per unit distance. It has been well documented in aqueous systems that LET can alter the relative effect of radiation dose such has a two-fold difference in generation of iron (III) in a de-aerated Fricke dosimeter for gamma rays vs. $^{10}B(n,\alpha)^{7}Li$ recoil particles [4]. Data collected from exposure to both gamma and alpha irradiation will be complementary to assessing the robustness of ligands as well as be useful for developing accurate models used for enhancing efficiency in industrial processes.

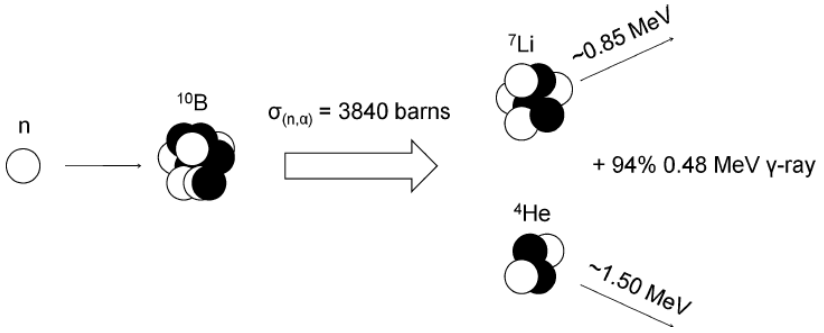

Figure 1. The neutron induced high LET radiolysis reaction

In this work we have investigated the effects of high LET radiation on TBP using the $^{10}B(n,\alpha)^{7}Li$ reaction (Figure 1) to create high energy particles analagous to alpha radiation emitted from used nuclear fuel. This method was studied in our previous work [5] and it was shown that high LET doses to both aqueous and organic samples can be administered by this method. Furthermore, this method has potential to overcome certain limitations of studying alpha radiation with ion accelerators and radioactive isotopes which may include confluent deposition and quantity of dose, experimentally isolating radiolytic effects from hydrolysis catalyzed by the presence of metals, and availability of equipment permitted to handle radioactive samples. Although information gleaned from these experiments is of a more fundamental nature since the isotopes and acid phase are absent, it will be useful for providing insights into the chemistry occurring in the presence of high LET radiation.

2. Experimental

A solution of 1 molar tributyl phosphate in n-dodecane was prepared for irradiations. This solution was specifically studied to model the organic phase of the PUREX process and degradation to the extraction reagent TBP by radiolytic attack. This study was on the organic phase only as done previously by several different research groups, e.g. by Holland et al. [6]. No acidic or aqueous phase was present during the irradiation nor was the organic solution pre-equilibrated with such a phase. These solutions were irradiated in the presence of gamma rays from an external ^{137}Cs source and high LET particles produced from boron activation during exposure to thermal neutrons in the UCI TRIGA reactor.

2.1. Gamma Irradiation: Low LET

A cesium-137 gamma cell (Cs137 Irradiator Mark-I, Model 68, J.L. Shepherd & Associates) was used for gamma irradiations. Different positions within the cell were characterized for doserate utilizing Fricke solutions. Fricke solutions containing 1 mM Fe(II), 1 mM NaCl and 0.4 M H_2SO_4 were aerated by bubbling air through them for a minimum of 30 min. Calibration standards of varying concentrations of Fe(III) in 1 mM NaCl and 0.4 M H_2SO_4 were prepared. The iron(II) sulphate heptahydrate and ferric ammonium sulphate dodecahydrate (Fe(III)) were both of ACS certified grade and obtained from Fisher Scientific. The sodium chloride was from standardized stock solutions in our laboratory made from filtered and recrystallized NaCl obtained from Fisher Scientific. The sulfuric acid was prepared from concentrated H_2SO_4 (17.8 M) and was obtained from EMD Chemicals.

Fricke solutions were placed in the cell and exposed to gamma radiation for different periods of time and at different distances from the center source to prepare calibration curves of the dose rates inside the cell. The solutions were analyzed for their Fe(III) content using a UV–VIS spectrometer (Ocean Optics JAZ), using 1 cm quartz cuvettes, by observing the characteristic peak at 304 nm. The solutions of varying concentrations of Fe(III) were measured prior to the unknown samples to verify linear calibration in agreement with the Beer-Lambert law.

All doses to organic samples irradiated in this study are reported with respect to the Fricke dosimeter. We refrained from making a correction for dose to organic solutions based on electron densities for example, so that a method of choice for making such a correction could be left to the observer or user of this data. It is acknowledged, however, that there will be subtle differences in dose to the Fricke solutions as compared to the organic solutions studied.

Solutions of 1 molar TBP in n-dodecane were degassed with nitrogen and irradiated at various distances from the source for varying durations. Solutions were removed and analyzed on an HP 5890 gas chromatograph utilizing an Agilent DB-1301, 30 m, 0.32 mm, 1.00 μm capillary column. The oven was programmed from 60 ^{o}C to 280 ^{o}C at a rate of 10 ^{o}C/min. Using standards of tributyl phosphate (Acros 99%), dibutyl phosphate (Aldrich 97%), monobutyl phosphate (MP Biomedicals LLC, no assay provided), and phosphoric acid (SAFC 85 wt% in water), residence times for these compounds were confirmed with flame ionization, flame photometric detection with a phosphorus filter, and mass spectrometry. Dibutyl phosphate, monobutyl phosphate and phosphoric acid required derivatization prior to GC analysis. Samples were esterified with diazomethane from a diazomethane generator kit (Aldrich), diazald (Aldrich 99%), carbitol (SAFC), ethyl ether (EMD Chemicals), and potassium hydroxide (Fisher Scientific).

2.2. $^{10}B(n,\alpha)^{7}Li$ Irradiation: High LET

For high LET irradiations, samples containing aqueous or n-dodecane-soluble boron compounds were placed in a sample carousel (lazy-susan) next to the core of the UC Irvine 250 kW TRIGA Mark I reactor. To

characterize high LET dose to a sample, Fricke solutions containing 1 mM Fe(II), 1 mM NaCl and 0.4 M H_2SO_4 with varying concentrations of boric acid (0–0.9 M) (Fisher Scientific) were prepared and irradiated at 500, 1,000, 2,000 and 3,000 W, respectively for 7 min[7]. Fricke solutions were put in sealed containers (NAA grade high density polyethylene obtained from LA Container Inc). The estimated neutron flux in the carousel positions is $3x10^9$ neutrons/cm^2-s at 1,000 watts. More details of these experiments can be found in previous work from our group [5].

To confirm linearity boron activation and high LET dose over the full operating range of the reactor up to 250 kW, additional samples were transferred into the reactor core operating at critical powers of 10 kW, 50 kW, 100 kW, 150 kW, and 250 kW via a pneumatic transfer line. More details for these experiments can be found in other work from our group [8].

Solutions of 1 molar TBP in n-dodecane were degassed with nitrogen and irradiated with bis (pinacolato) diboron (Aldrich 99%) at concentrations of 0 M, 0.115 M, 0.175M, and 0.23M for 3 hours at 250 kW. The estimated neutron flux in the carousel positions is $8x10^{11}$ neutrons/cm^2/s at 250 kW.

3. Results

3.1. Gamma Irradiation: Low LET

Results for TBP degradation and DBP formation during the gamma irradiation are shown in Figure 2a. Samples were analyzed for possible degradation products using GC and although monobutyl phosphoric acid (MBP) and phosphoric acid were detected, the concentrations were too small for a proper evaluation.

The data in figure 2a show that as TBP degrades DBP grows in, which is in line with previous studies. The mass balance between TBP and DBP does not add up which indicates that there are other degradation products formed directly by TBP as well as from the degradation of DBP.

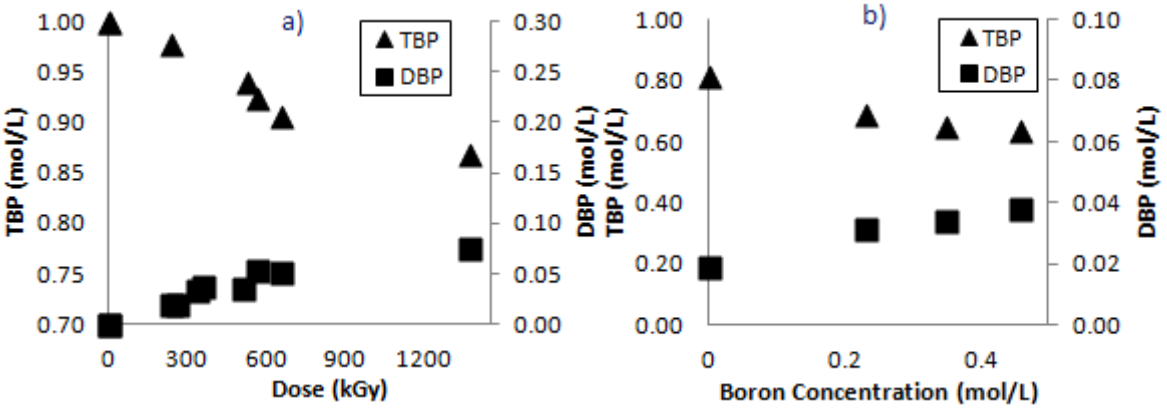

Fig. 2. a) Gamma (low LET) irradiation of 1M TBP in n-dodecane, b) High LET irradiation of 1M TBP in n-dodecane. Note the two separate scales for TBP and DBP concentrations, and the different range of the axis in figures a and b. Reactor samples were tested in triplicates, and uncertainties were ±2mmol/L for DBP and ±20mmol/L for TBP.

3.2. $^{10}B(n,\alpha)^7Li$ Irradation: High LET

From the irradiations of Fricke solutions containing boric acid, a relationship for doserate per boron concentration vs. reactor power was obtained for irradiating samples in the lasy susan irradiation position (Figure 3) [5].

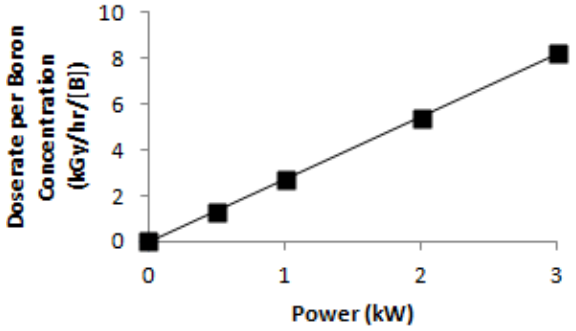

Figure 3. High LET dose rate per boron concentration vs. reactor power, figure reproduced from data [5].

Because dose rate is dependent on the neutron flux and the neutron flux is directly proportional to the reactor power the assumption was made that the linear relationship in figure 3 would be valid at all power levels in the UCI reactor, up to the maximum of 250kW. This has been confirmed in recent studies in our lab and is presented in a separate study [8]. The other assumption that was made is that the doserate to water (Fricke solutions) for high LET is directly comparable to the doserate to organic solvents since the high LET particles will deposit all their energy in the sample. Thus the relationship from figure 3 is directly applicable to the organic solutions containing TBP and bis (pinacolato) diboron.

Data for DBP formation and TBP degradation in the presence of high LET radiation are shown above in Figure 2b. Again, due to low concentration of MBP and phosphoric acid in the samples, these data are not quantifiable at this time.

Figure 2b clearly shows that as boron concentration in the sample is increased (i.e. high LET dose to the sample is increased) the degradation of TBP and formation of DBP is increased.

4. Discussion

Previous studies performed with this method evaluated methyl red degradation in the presence of low and high LET radiation and showed a notable difference between the two domains[5]. Application of this method to TBP was anticipated that it would reveal a similar relationship. Indeed, as seen in Figure 4, the slopes are different for low and high LET indicating different rates of formation of DBP as the dose increases.

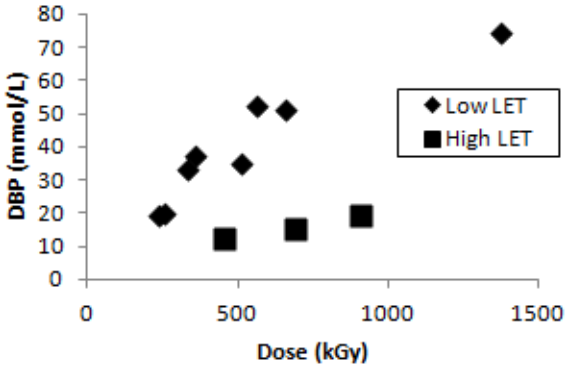

Fig. 4. Low LET vs. high LET formation of DBP. Formation of DBP in the reactor normalized for high LET only.

These differences which have been noted in other studies as well [9-10] are explained by the density of the ions formed in the alpha radiation track which is larger than that from gamma radiation. This large density reduces the amount of radicals that are free to escape and interact with extraction reagents. [11]

Future experiments will include more extensive study with more data points. Mass balances will be fit to these data from which rate constants and g-values for degradation and formation of TBP and DBP respectively will be calculated. These will be compared to gamma and alpha results published in the literature. For gamma, Holland et al. [6] found a g-value of about 0.31 μmol/J for g-DBP in 1 molar TBP/n-dodecane. In the Mincher et al. review [1] a range of g-DBP values were documented from 0.05-0.5 μmol/J for TBP/alkane solutions both in the absence of an aqueous phase and for some that were water saturated. We anticipate our g-DBP for gamma will be within the range of these published values. With respect to alpha, one study using ion beam measurements found no difference between the g-DBP from alpha and gamma [2] however, in light of other publications which have seen a difference between alpha and gamma irradiations of their respective systems[5, 9-10] we anticipate that future high LET studies will follow the same pattern seen in Figure 4. We will also repeat these experiments in the presence of an acidic aqueous phase with and without bound/solvated non-radioactive metal isotopes which is more representative of the solvent extraction process.

5. Conclusion

A solution of 1M TBP in n-dodecane was irradiated in the presence of both high and low LET radiation to quantify and compare TBP degradation and DBP formation. Low LET radiation was from an external ^{137}Cs source. High LET radiation was provided *in situ* from $^{10}Boron$ activation in a neutron field. Data show a decreased formation of DBP for high LET radiation vs. gamma radiation. Understanding the degradation of extraction reagents due to radiolytic attack is useful for assessing their robustness and modeling industrial and pilot scale processes to increase efficiencies. Continued studies using the method will include details of formation and degradation constants for high and low LET radiation for various solvent extraction reagents.

Acknowledgements

The authors would like to kindly thank the US Department of Energy and Nuclear Energy University Programs (NEUP project no. DE-AC07-05ID14517) for financial support. We would also like to thank the Atalante 2012 Conference organizers for their generous support offered for presenting of this material through an ACTINET-I3 Travel Grant.

References

[1] Mincher BJ, Modolo G, Mezyk SP. Review article: the effects of radiation chemistry on solvent extraction: 1. Conditions in acidic solution and a review of TBP radiolysis. *Solvent Extr Ion Exch* 2009;**27**:1–25.

[2] Ladrielle T, Wanet P, Lemaire D, Apers DJ. Alpha and gamma induced raiolysis of tributyl phosphate. *Radiochem Radioanal Lett* 1983;**59**:355-364.

[3] Lloyd MH, Fellows RL. Alpha radiolysis and other factors affecting hydrolysis of tributyl phosphate. 1985 In: Report ORNL TM-9565; Order No. DE85015071, Oak Ridge National Laboratory

[4] Choppin G, Liljenzin J, Rydberg J. *Radiochemistry and nuclear chemistry*. Woburn, MA: Butterworth-Heinemann; 2002

[5] Pearson J, Jan O, Miller GE, Nilsson M. Studies of high linear energy transfer dosimetry by $^{10}B(n,\alpha)^{7}Li$ reactions in aqueous and organic solvents. *J Radioanal Nucl Chem* 2012;**292**:719-729.

[6] Holland JP, Merklin JF, Razvi J. The radiolysis of dodecane-tribtyl phosphate solutions. *Nuclear Instruments and Methods* 1978;**153**:589-593.

[7] Schuler H, Barr NF. Oxidation of ferrous sulfate by ionizing radiations from (n,α) reactions of boron and lithium. *J Am Chem Soc* 1956;**78**:5756-5762.

[8] Pearson J, Wariner A, Jan O, Miller GE, Nilsson M. In preparation for publication.

[9] Bibler NE. Gamma and alpha radiolysis of aqueous solutions of diethylenetriaminepentaacetic acid. *J Inorg Nucl Chem* 1972;**34**:1417-25.

[10] Magnuson D, Christiansen B, Malmbeck R, Glatz JP. Investigation of the radiolytic stability of a CyMe4-BTBP based SANEX solvent. *Radiochim Acta* 2009;**97**(9):497-502.

[11] LaVerne JA, Chang Z, Araos MS. Heavy ion radiolysis of organic materials. *Radiat Phys Chem* 2001;**60**:253-7.